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Influence of heating rate on two-step sintering behaviour of different hydroxyapatite nanopowders

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INTRODUCTION

Producing of dense nanostructured calcium phosphate-based bioceramics represents a challenging issue in biomaterial science. High volume fraction of energetically rich grain boundaries contributes to improved attachment of chemical species, which are important in the processes of bone tissue regeneration. Beside that, nanostructured ceramics exhibited better mechanical properties due to changed fracture path. The process of presureless sintering is the most compatible route for industrial fabrication of dense bioceramic materials, but it is often connected with accelerated grain growth in final sintering stage. In the method of two-step sintering (TSS) the difference between kinetics of grain boundary diffusion and grain boundary migration is used to obtain almost full dense, nanostructured ceramics. However, designing of proper sintering parameters is very important in every sintering technique employed.

In this study, hydroxyapatite nanopowders were synthesized by different methods, precisely, hydrothermal processing of precipitate and chemical precipitation. The prepared powders were pressed in pellets and heated with different heating rates, with short isothermal dwell at certain temperature range. From that shrinkage curves the appropriate conditions were selected to design TSS experiments. The impact of heating rate on final density, phase composition, average grain size and microstructural uniformity is discussed.

EXPERIMENTAL PART

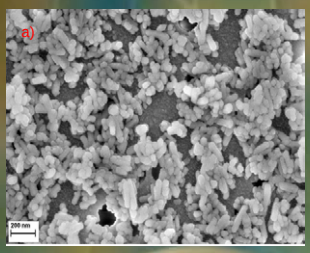
The starting chemicals used for the synthesis were $Ca(NO_3)_2$ $4H_2O$, 85 % H_3PO_4 and 25 % NH_4OH. The solution containing phosphate ions was added dropwise to the solution of calcium ions, under effective stirring, at T= 50 °C, while pH was adjusted to 11 by the addition of ammonia. The white precipitate obtained was subsequently treated in different ways. HAp 1 was produced by hydrothermal treatment of the precipitate at 200 °C. After reaching that temperature, the reaction mixture was quenched to the room temperature, washed to neutral conditions and filtrated. HAp 2 was produced by by boiling the precipitate for 10 min, aging of suspension for 24 h, filtrating, washing to pH=7 and drying overnight at 60 °C. All produced powders were characterized in order to determine the phase compostion,, morphology and specific surface area (SSA) by XRD, SEM and the BET method, respectively.
The synthesized powders were calcinated, uniaxially compacted at 400 MPa into 6 mm Ø pellets. The sintering was performed via conventional sintering in order to find out the best conditions for TSS.

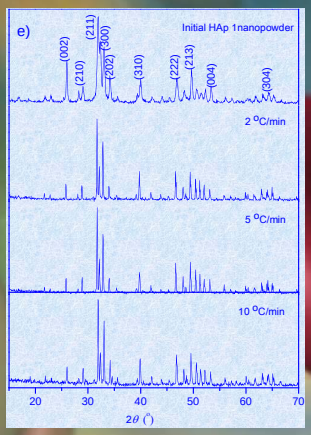
RESULTS AND DISCUSSION

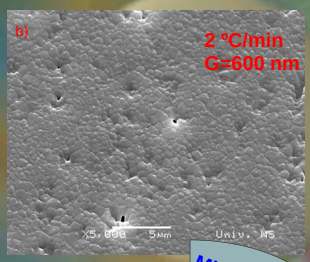
The obtained results are presented in the Table 1. SEM analysis of Hap 1 and Hap 2 nanopowders, together with TSS processed ceramics and its corresponding XRD patterns, are presented on Fig. 1 and Fig 3., respectively. Fig. 2 represents the dependance of the average grain size for HAp 1 nanopowder on heating rate.
It should be noticed that HAp 1 nanopowder exibited higer crystallinity and lower agglomeration degree than HAp 2, which resulted in lower sintering temperatures for HAp 1.

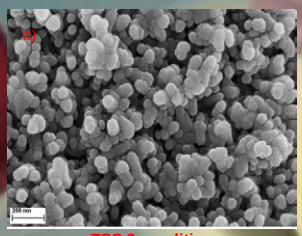
Table 1. Characteristics of synthesized powders and conclusions from sintering experiments.

Synthesized powder	HAp 1	HAp 2
Phase composition	Hydroxyapatite	hydroxyapatite
Morphology/Particle size(nm)	Elongated/ lenght~100,width~50	Spherical/ 55
SSA(m^2g^{-1})	51	72
Does transformation of HAp to β-TCP occur during heating?	YES	NO
Does heating rate change influence microstructural characteristics?	YES	NO

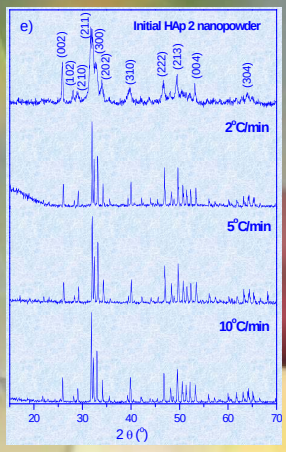






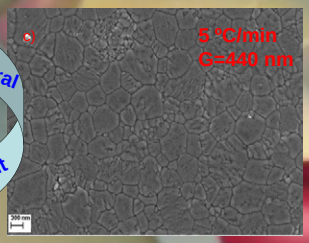


TSS 2 conditions:
T_1=1250 °C, t_1=5 min,
T_2=1150 °C, t_2=20 h;



Microstructural refinement

TSS 1 conditions:
T_1=1150 °C, t_1=5 min,
T_2=1050 °C, t_2=20 h;



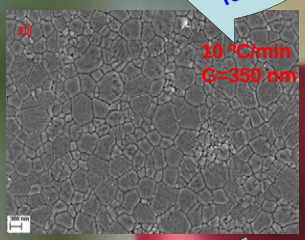


Fig. 1. SEM micrographs of: a) HAp 1 nanopowder and sintered ceramics via TSS 1 cycle by following heating rates b) 2, c) 5 and d) 10 °C/min; e) XRD patterns of these systems;

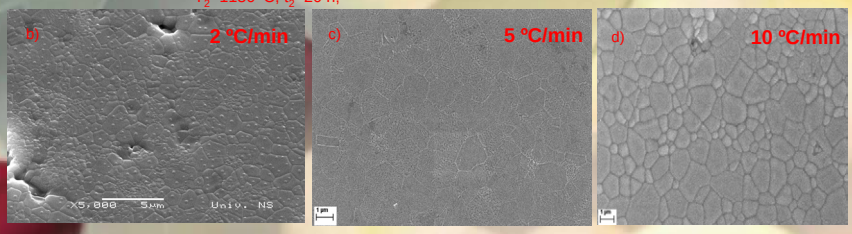


Fig. 1. SEM micrographs of: a) HAp 2 nanopowder and sintered ceramics via TSS 2 cycle by following heating rates b) 2, c) 5 and d) 10 °C/min; e) XRD patterns of these systems;

Grain size decrease

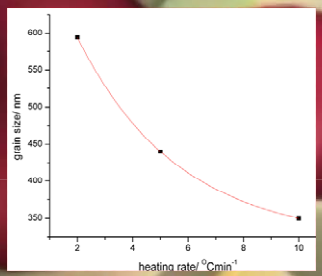


Fig. 2. Grain size change with heating rate in TSS 1 experiment;

CONCLUSION

1. Nanostructural HAp could be synthesized via both hydrothermal processing, HAp 1, and chemical precipitation, HAp 2.
2. The sintering behaviour is significantly influenced by powder characteristics and degree of agglomeration. HAp 1 could be sintered to full density at lower temperatures than HAp 2, indicating better sinterability of hydrothermally obtaind material.
3. TSS method is useful approach in sintering nanopowders, leading to preserved fine-grained microstructure. However, starting powders characteristics are of the great importance.
4. In the systems *occuring phase transformation from HAp to β-TCP, heating rate strongly affects micrustructural uniformity and grain size*, but the final density, too. For HAp 1 nanopowder, by increasing heating rate from 2 to 10 °C/min, the average grain size is almost 50 % decreased, following first order exponential decay. If there is no detectable phase transformation, no significant microstructure changes were observed, HAp 2.

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